INVESTIGATING THE INTERFACIAL COMPATIBILITY AND ADHESION OF COIR FIBRE COMPOSITES

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1 Introduction

The interest of using natural fibres in composite materials has greatly increased over the past decades thanks to their good mechanical properties in combination with environment-friendly characteristics. Among natural fibres, coir fibres are not very strong and stiff, but have high strain to failure which may increase toughness of some brittle matrices when they are used in composites [1]. In order to achieve a good performance of composite materials, it is important to understand the quality of the interfacial adhesion between fibres and matrices.

Generally, the adhesion at the interface can be described by following main interactions: physical adhesion, which also controls wettability of the fibre and the matrix; chemical bonding and mechanical interlocking created on rough fibre surfaces [2]. Good interfacial adhesion initially requires a good wetting between the fibre and the matrix, to achieve an extensive and proper interfacial contact; and the wettability mainly depends on the surface energy of the two materials. High surface energy of both fiber and matrix contributes to a high work of adhesion, while the matching of surface energy components results in a good fibre-matrix interfacial compatibility. These interactions are mainly controlled by the functional groups on the surface of the fibre and the matrix at the interfacial contact area.

The aim of this work is to study the interfacial adhesion of untreated and treated coir fibre composites with both polypropylene and epoxy matrices. Wetting measurements are carried out to determine the contact angles of fibres and matrices in various test liquids, which are used to estimate the surface energies. The fibre-matrix work of adhesion and interfacial tension are calculated to predict the compatibility and physical adhesion of the composites. Besides, fibre surface chemistry is studied by X-ray photoelectron spectroscopy (XPS) to have more information about functional groups at the fibre surface. Transverse flexural three-point bending tests are performed on unidirectional composites to determine interfacial strength, to examine the interface quality.

2. Materials and Methods
2.1. Materials

Fibres
Vietnamese coir fibres used in the study were extracted from the husk shell of coconuts with a purely mechanical extraction process. The fibres were then soaked in hot water at 70^0C for 2h, washed with ethanol, rinsed with deionized water and dried in a vacuum oven at 90°C. These fibres are named untreated coir fibre in this work. The treated coir fibres were obtained using 5% NaOH solution for 2h at room temperature, then washed thoroughly with deionized water and dried in a vacuum oven as described above. The alkali treatment was expected to remove wax and fatty substances on the untreated fibres.

Matrices
Both thermoplastic and thermoset polymer were used as matrices for untreated and treated fibres, namely polypropylene and epoxy. The polypropylene (PP) film was supplied by Propex, while the epoxy Epikote 828 and hardener Diaminocyclohexane were used.

2.2 Wetting measurements and fibre surface characterization

Contact angle measurements
Contact angle measurements of the coir fibers were carried out using the Wilhelmy technique, which allows to determine dynamic contact angles of various test liquids on the fibres. In order to obtain the static contact angle, the molecular-kinetic theory (MKT) was used to model dynamic wetting of the fibres following Eq.1. By using experimental data of dynamic angles, the static angle can thus be determined [3]. More details were also shown in a related study of the fibres [4].

$$v = 2K_0\lambda\sinh\left[\frac{\gamma_{LV}\left(\cos\theta_0 - \cos\theta\right)}{2nk_BT}\right] \tag{1}$$

For the matrices, the equilibrium contact angles of PP and cured epoxy were estimated from their advancing and receding angles, which were measured using the Wilhelmy method. Eq.2 was used for the calculation of the equilibrium angles.

$$\cos\theta_{eq} = 0.5\cos\theta_{ad} + 0.5\cos\theta_{re} \tag{2}$$

Estimation of surface energy and work of adhesion
Surface energies comprising polar and dispersive components of the fibres and matrices were estimated by the Owens-Wendt approach using the data of static equilibrium contact angles of various test liquids on the fibre and matrix samples [4]. Once the surface energies of the fibres and the matrices are known, it is possible to evaluate the work of adhesion of each composite system using the geometric mean approach introduced by Owens-Wendt as shown in Eq. 3.

$$W_a = 2\left(\sqrt{\gamma_{SV}^d\gamma_{LV}^d} + \sqrt{\gamma_{SV}^p\gamma_{LV}^p}\right) = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \tag{3}$$

Fibre surface characterization using XPS
To examine the surface chemistry of the untreated and the treated coir fibres, XPS analyses are performed. The analyzed area of the fibre surface was 700 μm x 300 μm, where the surface atomic composition, in terms of overall carbon, oxygen, nitrogen and silicon, is determined. The spectral deconvolution of C(1s) is also conducted.

2.3 Flexural mechanical tests of UD composites

Three point bending tests (3PBT) are performed on UD composites in both transverse and longitudinal directions following ASTM D790-03. When the UD composites are tested with the fibres in transverse direction, the matrix and interface properties will dominate the final composite properties. Therefore, the interface quality of the composites can be characterized.

3 Results and discussions

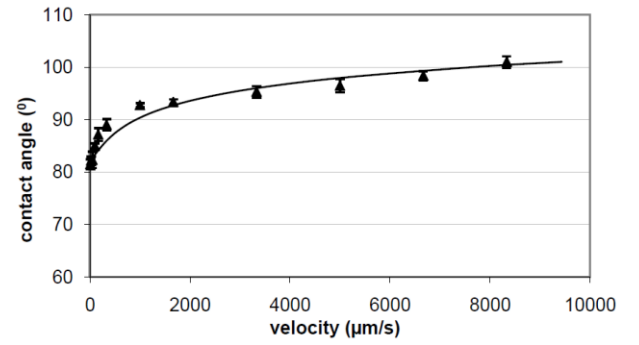### 3.1 Contact angles, surface energies and work of adhesion

Fig. 1. Advancing static contact angle of untreated coir in water obtained by fitting dynamic contact angle data with MKT.

Fig.1 shows the dynamic contact angles of untreated coir fibres in water are velocity-dependent reflecting the effect of angle hysteresis. By fitting the dynamic angles with MKT, the static contact angle can be obtained. The same fitting procedure was applied for both untreated and treated fibres in four different liquids (water, diiodomethane, ethylene glycol and formamide). The results of the static contact angles following the MKT curves are presented in Table. 1.

Table 1. Static/Equilibrium contact angles of untreated and alkali treated coir fibres in water (H2O), Diiodomethane (DIM), Ethylene glycol (EG) and Formamide (FM)

Fibre/Matrix	Static/equilibrium contact angle (^{0})			
	H_2O	DIM	EG	FM
Untreated coir	77.3 ± 0.3	48.2 ± 0.3	47.1 ± 0.5	47.7 ± 1.2
Treated coir	70.9 ± 1.1	51.5 ± 0.5	41.9 ± 1.2	40.2 ± 0.7
PP	85.9 ± 2.6	57.4 ± 2.7	60.5 ± 3.1	71.8 ± 2.5
Cured epoxy	74.6 ± 3.9	55.9 ± 2.5	52.4 ± 3.8	50.2 ± 2.3

Surface energies of the fibres and matrices are estimated and shown in Table.2. It can be seen that the untreated fibres seem to be hydrophobic with a low polar fraction of the surface energy. Moreover, 5% alkali treated fibres have higher surface energy with an increased polar fraction. For the matrices, the surface energy of polypropylene is quite similar to reported values in literature, while lower surface energy of cured epoxy is obtained in this work [6,7].

Table 2. Surface energies comprising polar and dispersive components of coir fibres and matrices.

Fibre/Matrix	Surface free energy (mJ/m^2)		
	total	dispersive	polar
Untreated coir	40.4 ± 3.9	35.1 ± 3.6	5.3 ± 1.5
Treated coir	42.2 ± 4.2	33.5 ± 3.7	8.7 ± 2.0
PP	30.7 ± 4.0	27.1 ± 3.7	3.6 ± 1.4
Cured epoxy	37.3 ± 4.6	29.6 ± 4.0	7.7 ± 2.2

The calculated work of adhesion for each composite system (Table 3) shows the improvement of alkali treatment on the adhesion of the epoxy composite, which can be partially attributed to the higher surface energy and polar component of the fibres. For the PP there is also a small positive effect on adhesion strength, but this must be attributed to some cleaning and/or fibre surface roughening effect of the alkali treatment. The interfacial energy, γ_{SL}, depending on the matching of surface energy components of fibre and matrix, also has an influence on the work of adhesion. Lower interfacial energy contributes to higher work of adhesion. As such, interfacial energy should be minimised to increase the thermodynamic stability of the interface.

3.2 Fibre surface chemistry

In Fig. 2, typical results of C 1s spectra for untreated and treated coir are compared. The C 1s peak is decomposed into four sub-peaks C1–C4 representing: carbon solely linked to carbon or hydrogen C–C or C–H (C1), carbon singly bound to oxygen or nitrogen C–O or C–N (C2), carbon doubly bound to oxygen O–C–O or C=O (C3) and carbon involved in ester or carboxylic acid functions O=C–O (C4). For both untreated and treated coir fibres, C1 is higher than C2–C4. The high value of C1 indicates the presence of un-oxidised carbon atoms at the surface, which can be attributed to high percentage of hydrocarbon on the fibre surface. In the untreated coir, the high proportion of C1 carbon suggests a combination of hydrocarbon rich waxes and lignin. This is supported by the low proportion of C2–C4. The treated fibre shows lower C1 and
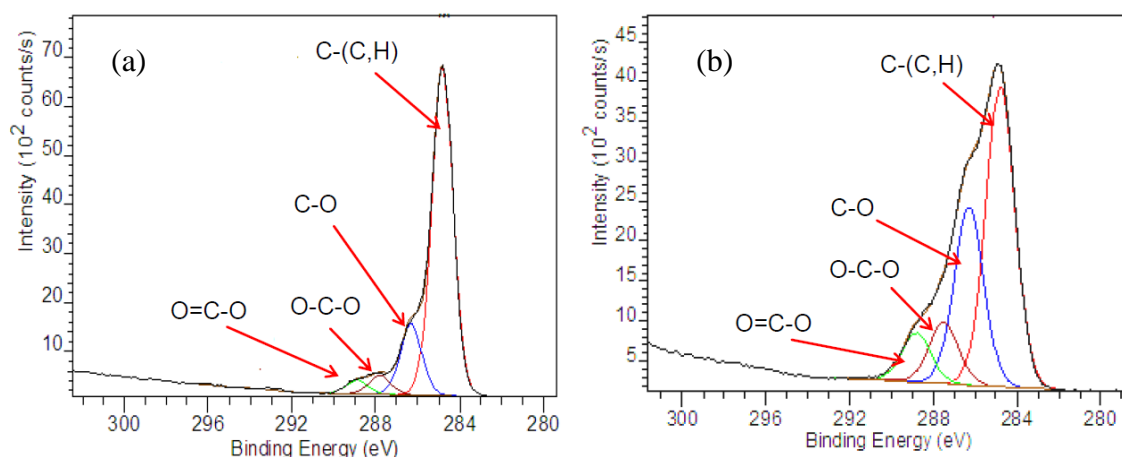

Fig.2. Typical C 1s spectra, decomposed into four components C1-C4 for (a) untreated coir (b) alkali treated coir
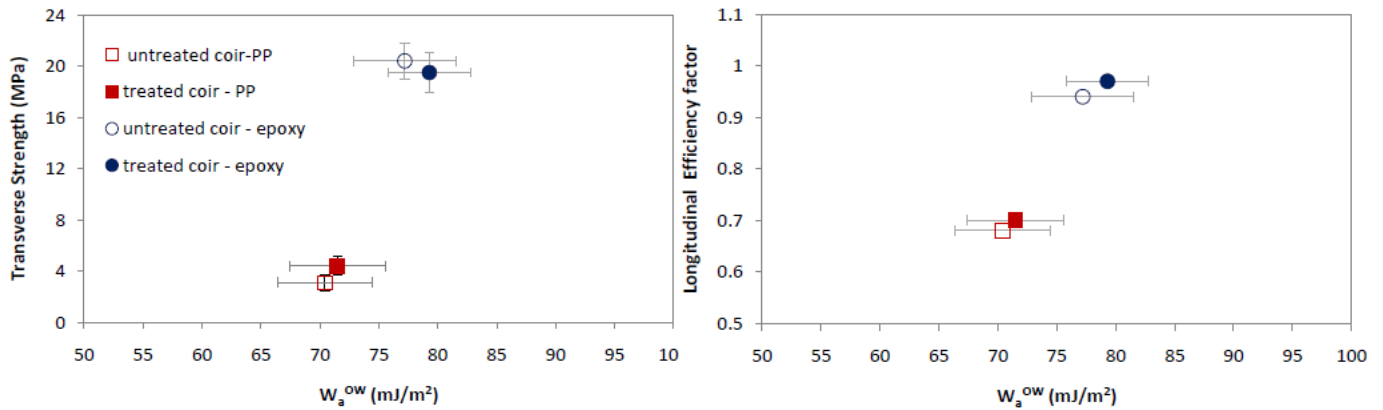
Fig. 3. Plots of interfacial strength and longitudinal efficiency factor vs work of adhesion for untreated and treated coir composites.

higher C2–C4 than in case of the untreated one. This suggests a larger amount of lignin present at the surface after removing the waxes by alkali treatment. A correlation is found in the result of the wetting measurements, where higher surface energy and polarity are determined after removing waxes by alkali treatment.

3.3 Fibre-matrix interfacial adhesion

Table 3. Work of adhesion, interfacial energy, transverse strength and efficiency factor of longitudinal strength of coir fibre composites

Composite	W_a (mJ/m^2)	γ_{SL} (mJ/m^2)	Trans. strength (MPa)	Eff. factor
Untreated coir /PP	70.4 ± 4.0	0.7	3.1 ± 0.6	0.68
Treated coir /PP	71.5 ± 4.1	1.4	4.4 ± 0.7	0.70
Untreated coir/epoxy	77.2 ± 4.3	0.5	20.4 ± 2.5	0.94
Treated coir/epoxy	79.3 ± 3.5	0.2	19.5 ± 1.6	0.97

The interfacial strength of UD composites measured by 3PBT in transverse direction is shown in Table 3. A better interfacial adhesion is seen for treated coir PP in comparison with untreated coir PP. Although there is a small improvement in the work of adhesion, the interfacial energy is somewhat increasing, which leads to the hypothesis that the improvement in adhesion may be due to cleaning or

surface roughening of the fibre. In case of coir epoxy, the transverse strength is similar in both untreated and treated fibre composites. From a SEM image of the failure surface (Fig.4), it can be observed that the fracture occurs with fibre breakage. Therefore, the transverse strength is not fully representative for the interface adhesion. Therefore, the efficiency factor of the longitudinal strength of coir epoxy UD composites is used to compare the influence of interfacial adhesion on the composite strength. The efficiency factor is the ratio of experimental longitudinal strength over the calculated value following the rule of mixtures. The results of efficiency factors in Table 3 and Fig.3 show the improvement of the interface and composite strength when the fibres are treated.

In conclusion, the results of composite interfacial strength are quite consistent with the results of the work of physical adhesion even if chemical adhesion mechanisms have so far not been considered yet. Especially for reactive epoxy, an important contribution from chemical adhesion may be expected.

In a next step, also 3-component models for surface energy determination (more particularly the acid-base theory) will be employed, to include the effects of surface charge in the analysis.
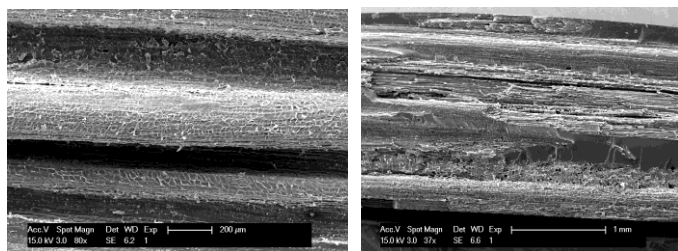
Fig. 4. SEM images of fracture surface in transverse 3PBT (a) coir PP (b) coir epoxy

4 Conclusions

Wetting analysis consisting of contact angle measurements and fibre surface energies estimations was conducted to predict composite interfacial compatibility and adhesion by means of work of (physical) adhesion and interfacial energy. In combination with the characterization of fibre surface chemistry, fibre surfaces can be studied and modified for use in composites.

In this study, there is an agreement between the results of the wetting analysis and those of composite interface mechanical tests.

Acknowledgments

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